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Project Summary

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Characterization of Boliden's Sulfide-Lime Precipitation System

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The Project Report summarized here provides information on the soluble sulfide precipitation process (Na_2S) used at a copper/lead smelter for treatment of wastewater. The study presents the results of a sampling study which aimed to define the process kinetics of a full scale plant. The generation of H_2S gas, metals removal, and sludge handling are discussed.

Excellent removal of most metals, including arsenic was shown. Process control problems prevented 99%+ removal of all metals, however.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Sulfide precipitation is an effective process for the treatment of industrial wastes containing highly toxic heavy metals. The attractive features of the sulfide precipitation process are: attainment of high degree of metal removals over a broad pH range, effective precipitation of certain metals (such as: As, Cu, Cd, Hg) even at very low pH, low detention time requirement in the reaction tank because of the high reactivity of sulfides, and the feasibility of selective metal recovery. With sulfide precipitation, the high reactivity of sulfides (S^{2-}, HS^-, H_2S) with heavy metal ions and the very low solubilities of the heavy metal sulfides over a broad pH range are features not found with the hydroxide precipitation processes.

Industries engaged in metal finishing or metal production operations use large quantities of contact process water, and the spent process wastewater streams contain moderate to high concentrations of As, Cd, Cu, Zn, Pb, Hg, etc. Various physico-chemical treatment methods to remove heavy metals have been reported in the literature. Hydroxide (lime) precipitation of heavy metals followed by settling of the precipitates is most often used to treat industrial wastewaters. However, the minimum solubilities for different metals occur at different pH values and the hydroxide precipitates are amphoteric in nature and thus maximum removal efficiency of mixed metals cannot be achieved at a single precipitation pH. Hydroxide precipitation of arsenic cannot be achieved at any pH value. Arsenic precipitation occurs only at very high pH when lime is used to form calcium arsenate.

Sulfide precipitation (with Na_2S or NaHS) is an effective alternate technology. Sulfide precipitation processes to remove heavy metals have gained considerable importance[1-8]. The overall objective of this investigation is to establish the effectiveness of the sulfide

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precipitation process for the treatment (metal removals and recovery) of wastewaters containing arsenic and various heavy metals. Arsenic separation behavior is particularly emphasized because of its importance in non-ferrous metal production wastewaters. The bench-scale experiments were conducted at the University of Kentucky and the *full-scale* (200 m^3/hour capacity) experiments were conducted with a unique system developed by a Swedish non-ferrous metal production (copper and lead smelter) company.

Sulfide Precipitation Reactions

Most heavy metal sulfides have very low solubilities, even at acidic pH values. HgS (solubility product = $10^{-52.4}$), AS_2S_3, CuS, CdS, and PbS can be completely precipitated even at pH 2, whereas ZnS (solubility product = $10^{-23.8}$) precipitation would be incomplete at pH < 4. The extent of metal sulfide precipitation is a function of pH, type of metal, sulfide dosage, and other interfering ions that might be present.

With divalent heavy metals the important metal — sulfide reactions are:

$$\begin{array}{ccc} & H_2S,\ HS^- & \\ & \downarrow\uparrow\ +H^+ & \\ M^{2+} + S^{2-} & \rightleftharpoons & MS\ (solid) \\ \downarrow\uparrow\ +OH^- & & \\ M(OH)^+,\ M(OH)_2,\ M(OH)_3^- & & \end{array}$$

For arsenic (As[111]) solutions, the sulfide reactions are more complicated because the metal exists as oxyacids and/or oxyanions. The primary reactions between As(111) and sulfide are listed in Table 1.

Figure 1 shows the calculated solubilities of various metal sulfides as a function of pH. The calculated values include all metal hydrolysis reactions. Arsenic precipitates only in acidic pH (pH < 5); the solubilities of other metals decrease with an increase in pH values. The solubility of metal hydroxide precipitates are also computed for comparison purposes. The metal hydroxide precipitate solubilites are considerably higher than the corresponding sulfide precipitates and the precipitation of hydroxide occurs only in a narrow pH range. With sulfide precipitation, a residual concentration less than 0.1 mg/l metal (for Cu, Cd, Pb, and Zn) could be achieved at 4 ≤ pH ≤ 12.

Experimental

Bench-Scale Studies. Laboratory studies were primarily conducted with actual scrubber wastewaters obtained from a non-ferrous metal production plant. Bhattacharyya, *et al.*[3] have reported the description of the experimental unit used for the bench-scale studies. The wastewater pH was first elevated to 4.0 to 5.5 with lime slurry, prior to the addition of Na_2S. Na_2S dosages of ≤ 1.0 x were used to establish the feasibility of arsenic separation (along with other heavy metals) at alkaline pH values (pH 8-9) by a combination limesulfide precipitation.

Full-Scale Studies. The full-scale data were obtained at Boliden Metall Corporation, Skelleftehamn, Sweden. The full-scale plant, which was put into operation in 1978, was designed to precipitate (at pH 3-5) As, Zn, Cu, Pb, Cd, and Hg as sulfide for possible recovery of metals by recycling to "roaster", and to remove fluoride separately by lime (at pH > 10) as CaF_2 for landfill. A schematic diagram of the process is shown in Figure 2. The wastewater was first partially neutralized (to pH 2.5-3.0) with NaOH, and then Na_2S (as 15% Na_2S solution) was added. The reagent dosages were controlled by monitoring pH. The sulfide precipitate was removed by sedimentation (after polymer addition) and post-filtration. The wastewaters treated also contained fluoride, which was removed by precipitation with lime (10% lime slurry) following sulfide precipitation. Five separate tests were used to determine the extent of removal of heavy metals and arsenic, and to establish the performance of the individual vessels (sampling points are shown in Figure 2). The process was evaluated after the plant had been in operation for about one year.

Table 1. Arsenic (III)-Sulfide Precipitation Reactions

Reactions	
$As_2S_3\ (s) + 4\ H_2O$	$2HAsO_2 + 2\ H_2S$
$HAsO_2$	$H^+ + AsO_2^-$
$2\ As_2S_3\ (s) + 2H_2O$	$3\ H^+ + As_3S_8^{3-} + HAsO_2$
$1/2\ As_2S_3\ (s) + 1/2\ S^{2-}$	AsS_2^-
$AsS_2^- + H^+$	$HAsS_2$
$H^+ + S^{2-}$	HS^-
$H^+ + HS^-$	H_2S

Results and Discussion

Bench-scale sulfide precipitation experiments were conducted with three actual scrubber wastes (Table 2) obtained from a copper smelting operation. The wastes contained high concentrations of heavy metals, iron and arsenic. Previous studies[3] with actual smelter effluents have shown that high heavy metal removal efficiencies can be achieved by precipitation with sodium sulfide followed by separation of the sludge from the clarified wastewater. Arsenic removal was dependent on the wastewater characteristics. Since arsenic precipitates only at low pH values (Figure 1) as AS_2S_3 and consumes 1.5 moles sulfide per mole of arsenic, this study was directed to establish the possibility of simultaneous removal of arsenic (by adsorption on precipitates or by Fe-As interaction) and heavy metals at alkaline pH values with Na_2S dosage ≤ 1.0 x. The theoretical sulfide dosage (one mole of sulfide for each mole of Cd, Zn, Fe, Cu, and Pb) in the absence of any AS_2S_3 formation is about 9.0 mM (288 mg/l S) for Batch I waste, 24.0 mM (768 mg/l S) for Batch II waste, and 30.0 mM (960 mg/l S) for Batch III waste.

Sulfide precipitation experiments with the three scrubber wastes (Table 2) were conducted after initial pH elevation with lime slurry) to 5.0 - 6.0. For pH adjustment, 1.4 to 1.8 g/l of $Ca(OH)_2$ was required. The sulfide precipitation reaction pH was varied between 7.5 and 8.5. The maximum metal separations in

all cases was obtained with 0.6X (60% of theoretical sulfide required to react with Cu + Zn + Fe + Cd + Pb) sulfide dosage and at a final pH around 8.0. At this pH, and with sulfide dosages less than 1.0X, both sulfide and hydroxide precipitates of metals (except arsenic) are formed and in this case the process is termed "Hydroxide-Sulfide Precipitation."

The metal separations obtained with Batch I and Batch II wastes were quite similar; but with Batch III waste the arsenic separation was considerably poorer than the results obtained with Batch I or Batch II wastes (Table 3). For both Batch I and Batch II wastes, 98-99.6% metal (including As) removals were obtained at 0.6X dosage and pH 8.0. With Batch III waste, variable sulfide dosage studies again indicated 0.6X to be optimum dosage, but arsenic removal was only 83%. Experimental efforts to increase arsenic removal are discussed below. The residual metal concentrations (at maximum achievable separations) obtained with the three wastes at the optimum operating conditions (sulfide dosage = 60% of theoretical and final pH of 8.0) are shown in Table 3.

Studies showed that the value of the molar ratio of Fe/As in the raw waste determined the extent of arsenic separation. In an effort to understand the effect of Fe^{+3} on arsenic separation, several experiments (at the optimum Na_2S dosage) were conducted with normal synthetic wastes (simulated Batch I type) and synthetic waste without Fe^{+3}. Both wastes contained 100 mg/l arsenic (similar to Table 2).

The following results at 0.6X Na_2S dosage and pH 8.0 show that arsenic removal dropped considerably in the absence of Fe^{+3} (primarily present as ferric hydroxide):

Waste	Molar $\frac{Fe}{As}$	Removal % As	Cd	Zn	Cu	Pb
Synthetic Batch I type waste	2.01	98.5	99.0	98.6	99.9	99.9
Synthetic Batch I type waste without Fe^{+3}	0	59.0	99.0	99.3	99.9	99.0

Synthetic (Batch I) waste gave all metal removal results the same as that of actual wastes (Table 3). With less than theoretical sulfide dosage, Fe^{+3} is precipitated as $Fe(OH)_3$ and thus enhances arsenic removal. The decrease in Fe/As ratio from 2.01 to zero caused arsenic separation to drop from 98% to 59%. The molar ratio of Fe/As for both Batch I and Batch II wastes were about 2.0 and arsenic removal was excellent (Table 3). The Batch III waste had a molar Fe/As ratio of 0.27 and arsenic separation was only 82%. By increasing the Fe/As ratio of Batch III waste to 1.0, arsenic separation increased to 99% (Figure 3). Figure 3 shows that arsenic removal is reduced at molar Fe/As less than 0.8. A different type of actual copper plant waste (Acid Plant Waste) containing 95 mg/l arsenic, 9.0 mg/l Fe, and other heavy metals (Cd, Zn, Cu, Pb), gave greater than 99% removal of all heavy metals (except arsenic) at the optimum sulfide dosage. The arsenic separation with this waste was only 40% because of the low molar Fe/As ratio (0.13) in the acid plant waste.

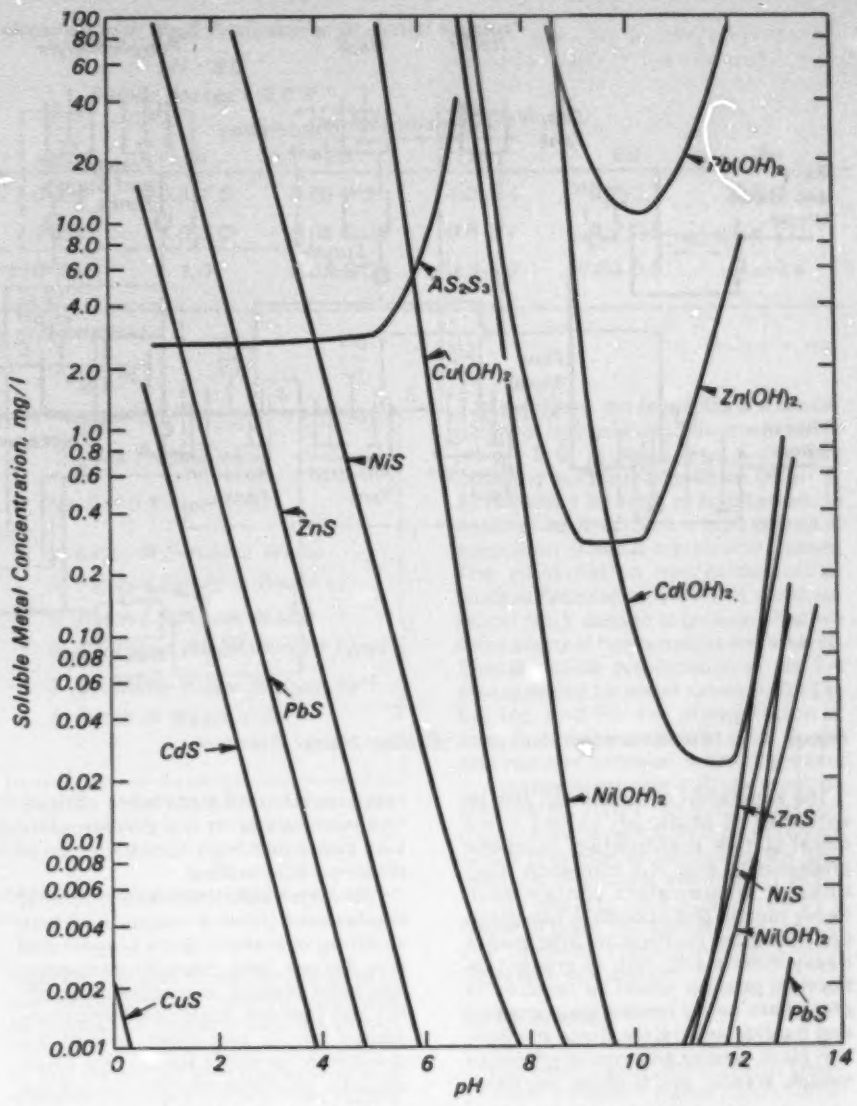

Figure 1. Calculated solubilities of metal sulfides and metal hydroxides.

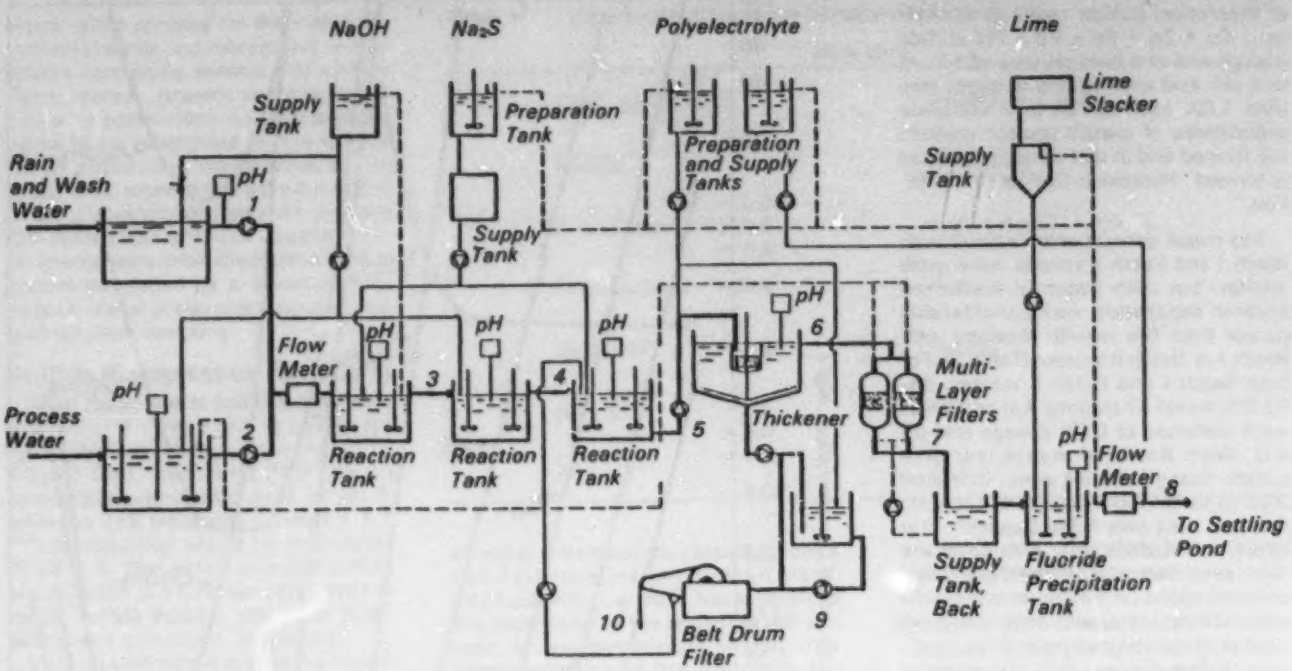

Figure 2. Sulfide precipitation plant (Boliden Mettal, Sweden).

The separation of metals can also be achieved at acidic pH values since metal-sulfide precipitation reactions predominate over H_2S formation reactions. If wastewaters contain both heavy metals and fluoride, a two-stage precipitation (sulfide to precipitate heavy metals and lime to precipitate fluoride) process would be required to precipitate heavy metals (plus arsenic) and fluoride separately. Since the Boliden plant wastewater contained heavy metals, arsenic, and fluoride, two separate precipitation steps were utilized. The wastewater at the Boliden plant also contained high concentration of dissolved SO_2 (sulfite).

The major constituents of the inlet wastewater (from a copper and lead smelting operation) were arsenic and zinc. Copper, lead, mercury, and selenium were present in smaller amounts. For the five full-scale test runs (conducted over a two-week period) the combined (process water and wash water) inlet concentration ranges are shown in Table 4. The process was evaluated by sampling at various points (sampling points are shown in Figure 2). The sulfide precipitation pH was in the range of 3.7 to 4.8 and the fluoride precipitation pH was in the range of 11.2 to 11.5.

Table 2. Analysis of Actual Scrubber Blowdown Waters from Copper Smelting Plant #A

Parameter	Concentration		
	Batch I	Batch II	Batch III
pH	1.65	1.80	2.80
As	100 mg/l	307 mg/l	612 mg/l
Se	3.0 mg/l	2.8 mg/l	1.5 mg/l
Cd	10.5 mg/l	12.0 mg/l	15.0 mg/l
Zn	86 mg/l	202 mg/l	175 mg/l
Cu	297 mg/l	792 mg/l	1600 mg/l
Fe	149 mg/l	441 mg/l	122 mg/l
Pb*	39 mg/l	142 mg/l	62mg/l
Hg	2.0 mg/l	1.5 mg/l	—
SO_4	700 mg/l	1300 mg/l	2700 mg/l

*91% of Pb is present as insoluble lead ($PbSO_4$)

The full-scale results of a typical run are shown in Figure 4. Hg, Cu, Cd, and Pb removals were complete by sulfide precipitation, whereas As and Zn separation was not adequate because of improper control of Na_2S dosage and pH. Since arsenic precipitates best around pH 3 and zinc precipitation is complete above pH 5, two-step precipitation would be most desirable. The overall removal of all metals was excellent, with sulfide precipitation followed by lime precipitation. The ranges of removal of metals by sulfide precipitation only (point 7 in Figure 2) and by sulfide-lime combination (point 8 in Figure 2) process are shown in Table 5 for the five full-scale tests.

The inadequate separations (by sulfide precipitation only) of As and Zn obtained in the full-scale tests were due to the wide fluctuations of pH and sulfide dosage (0.8 X to 3.1 X) and the consumption of a portion of the Na_2S

*Table 3. Residual Metal Concentrations Obtained with Na_2S Precipitation of Actual Wastes**

pH = 8.0
Sulfide dosage = 0.6 X

Waste	Sulfide Dosage	Concentration, mg/l					
		As	Se	Cd	Zn	Cu	Fe
Batch I	5mM (162 mg/l S)	1.0-2.0	0.5-1.0	0.06-0.2	1.0-1.4	0.1-0.2	0.5-0.8
Batch II	14mM (448 mg/l S)	1.0-2.5	1.0-3.0	0.05-0.08	0.8-1.1	0.2-0.5	0.4-0.5
Batch III	18mM (576 mg/l S)	110-150 (9.5)**	1.0	0.02-0.06	0.3-1.3	0.08-0.5	0.2-0.6

* filtered through 0.45 μ filter (after sulfide precipitation)
**at molar Fe/As = 1 (by adding Fe^{3+})

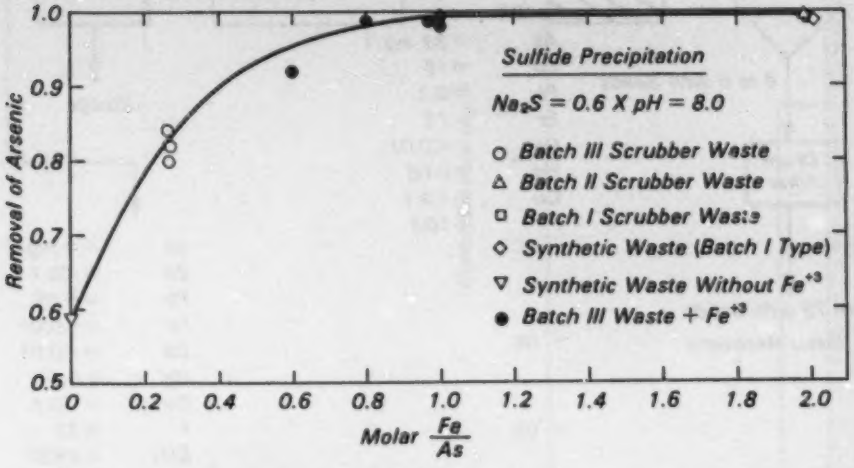

Figure 3. Effect of molar feed ratio of Fe/As on arsenic removal by a combination hydroxide - sulfide precipitation.

reagent by dissolved SO_2 (sulfite) present (Table 4) in the wastewater. The control technique of sulfide dosage by pH rise was found to be insufficient for simultaneous arsenic and zinc removal at optimal efficiency. In order to understand the importance of sulfite-sulfide side reaction at acidic pH values, bench-scale studies were conducted with single metal salts in the presence of sulfite at acidic pH values. Depending on the metals studied, part of the Na_2S was consumed by SO_3^{2-} to form elemental sulfur and thiosulfate. Even with sulfide overdoses at low pH values no H_2S gas loss from the solutions occurred (also observed in full-scale tests) due to SO_3^{2-} - H_2S reactions. At stoichiometric Na_2S dosages (to form AS_2S_3, ZnS, etc.) the sulfite-sulfide reaction played an important role only during precipitation of As and Zn at low pH values. The decrease in separation for As and Zn in the presence of sulfite is shown in Figure 5. For ZnS formation (because of low solubility product) the sharp increase in residual Zn concentration (as shown by cross-hatched area) and consumption of SO_3 (as shown by a decrease in SO_3 concentration) are evident from Figure 5. The effects of sulfide-sulfite reaction were found to be negligible above pH 5.

In summary, the feasibility of a combination of hydroxide-sulfide precipitation (at pH 8-9) process, and a process involving sulfide precipitation (at pH 3-5) followed by lime precipitation, is established to achieve a high degree of separation of heavy metals and arsenic. The combination hydroxide-sulfide process required only 60% of the theoretical Na_2S dosage to provide effective separations of heavy metals and arsenic. Simple sulfide precipitation at pH 3-4 also provided excellent removals for Cu, Cd, Hg, and Pb. For precipitation of arsenic and zinc sulfide at pH < 5, the side reaction between sulfite (if present in wastewater) and sulfide must be considered. Hydrogen sulfide gas formation was never found to be a problem during precipitation because of the high reactivity of sulfides and heavy metals.

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1. Lantz, J.B., "Evaluation of a Developmental Heavy Metal Waste Treatment System," *Naval Construction Battalion Center Report No. ER-314-40-6* (1979).

Table 4. Analysis of Inlet Wastewaters (Full-Scale Plant)

Parameter	Concentration, mg/l
pH	1.9-2.8
As	130-450
Zn	30-60
Pb	20-40
Cd	3-16
Cu	3-5
Hg	2-4
Fe	5-20
Sulfite (dissolved SO_2)	600-1000
SO_4	1500-2000
Fluoride (F)	90-130

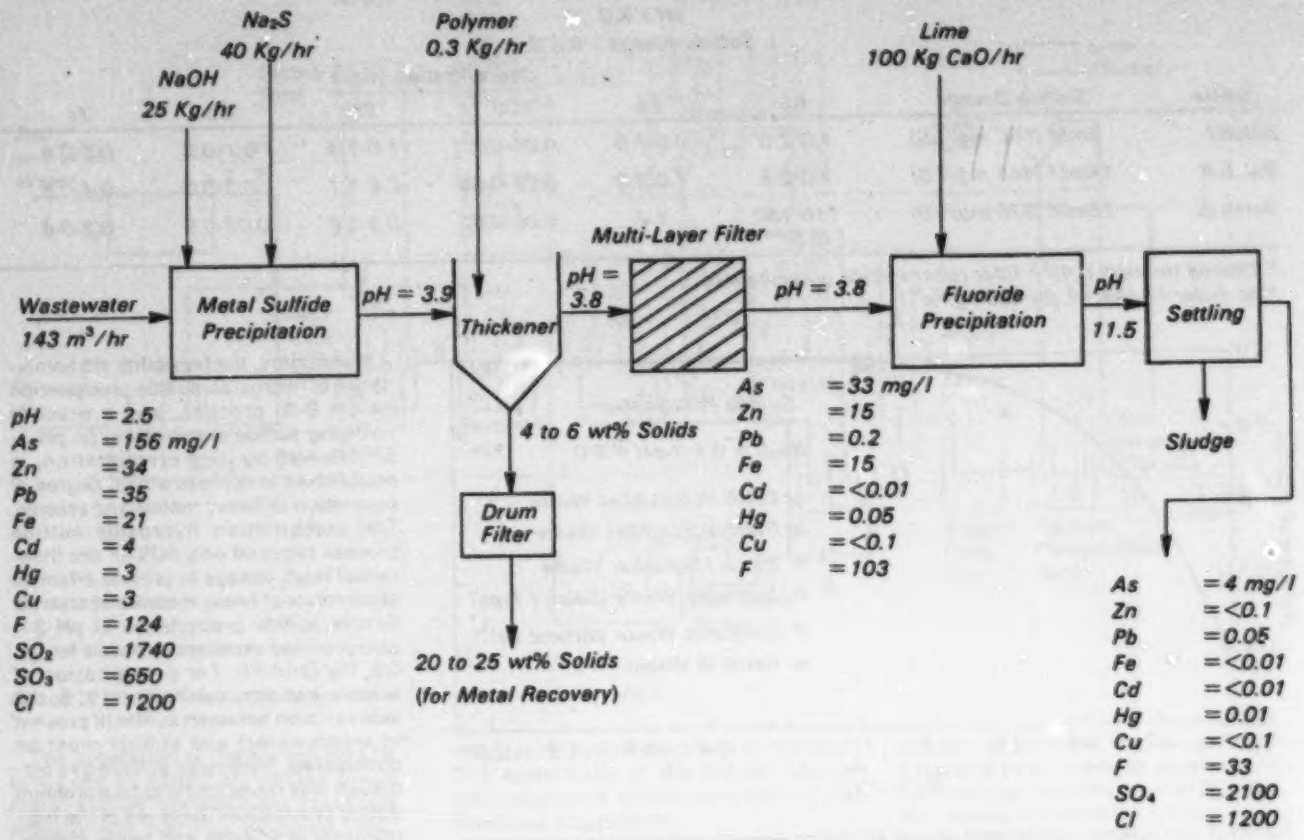

Figure 4. Typical residual metal concentrations obtained by full-scale test run [Boliden Metall].

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Table 5. Removal of Metals by Sulfide Precipitation and by Sulfide Precipitation Followed by Lime Precipitation (Full-Scale Process)

Component	% Removal	
	Sulfide Precipitation*	Sulfide + Lime Precipitation**
As	67-87	96-99
Zn	51-75	99
Pb	97-99	97-99
Cd	99	99
Cu	>90	>90
Hg	99	99
Fe	2-26	>99
Fluoride	0	70-78

*Sampling point 7 in Figure 2
**Sampling point 8 in Figure 2

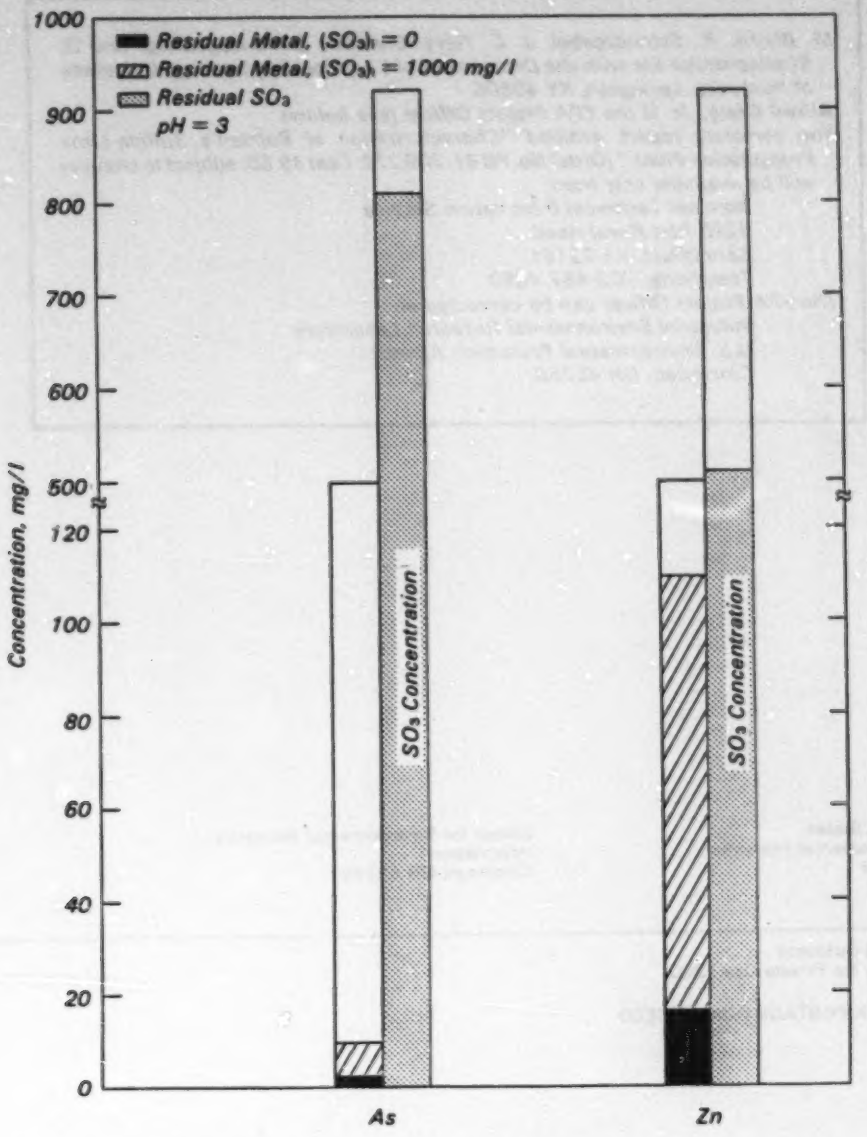

Figure 5. *Comparison of residual metal concentration and sulfite comsumption for 500 mg/l metal concentration at 1.0X Na_2S dosage.*

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Alfred Craig, Jr. is the EPA Project Officer (see below).
The complete report, entitled "Characterization of Boliden's Sulfide-Lime Precipitation Plant," (Order No. PB 81-209 272; Cost $9.50, subject to change) will be available only from:
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